

Improved correction method for using passive air samplers to assess the distribution of PCNs in the Dongjiang River basin of the Pearl River Delta, South China

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ABSTRACT

An improved correction method was established using passive air samplers to assess the distributions of polychlorinated naphthalenes (PCNs) in the eastern Pearl River Delta, South China. This method was based on a joint correction that used the active air sampling rate and the addition of deuration compounds. As a correction factor, the deuration compounds' properties do not need to be similar to the target compounds. The total PCN air concentrations ranged from 6.4 to 832, with an average of $148 \pm 201 \text{ pg m}^{-3}$ in the study area, while the TEQ of the PCNs ranged from 1.2×10^{-4} to $2.6 \times 10^{-2} \text{ pg m}^{-3}$. High concentrations of PCNs were mostly observed in the highly industrialized areas. The PCN air levels were remarkably increased in winter compared with summer. Tri-CN was the most dominant homologue group, while CN 24 was the most dominant congener. The high proportion of combustion-related PCNs suggests that the contribution of combustion sources to the PCN air burden has been significant recently in comparison with historical emissions.

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1. Introduction

Polychlorinated naphthalenes (PCNs) are a group of 75 congeners consisting of naphthalene substituted with 1–8 chlorine atoms. PCNs have been identified as persistent, toxic, and bio-accumulative substances (UNEP Chemicals, 2004). Historically, they were used for their thermal stability in dielectric fluids and insulators (Falandysz, 1998). PCNs have not been commercially produced since 1977, but they are still routinely observed in the environment (Helm and Bidleman, 2005; Baek et al., 2008; Mari et al., 2008). Evaporation from discharged or in-use products containing PCNs as well as release during waste, commercial, residential, agricultural, and other combustions are still sources for the addition of PCNs to the environment (Falandysz, 1998). Assigning the current contributions of PCNs to different sources is important because they have been banned.

Passive air sampler (PAS), a simple power-free device based on the theory of physical advection and diffusion, has been used for various monitoring research projects from regional to global scales to investigate the environmental levels and distributions of POPs (Shoeib and Harner, 2002; Pozo et al., 2004; Lee et al., 2007), for

which an active high volume air sampler is impractical for sampling at a high spatial resolution. Though PASs have been used to achieve spatially resolved data for almost a decade, they still have some shortcomings, such as the complex and limited sampling rate calculation. To use the PAS quantitatively to assess ambient air concentrations, it is necessary to know the sampling rate for the specific compounds. Those sampling rates were determined by the calibration exercises for different classes of chemicals, individually (Shoeib and Harner, 2002). Thus far, two primary methods are used to obtain the sampling rate: one uses an active air sampler (AAS) (Shoeib and Harner, 2002; Harner et al., 2006a; Baek et al., 2008), and the other uses the addition of deuration compounds (DCs, or performance reference compounds/PRCs) (Pozo et al., 2004; Gouin et al., 2005; Gioia et al., 2006; Pozo et al., 2006; Moeckel et al., 2009). DCs are semivolatile chemicals that neither exist in the environment nor interfere with the analysis of target compounds, so they are added to the PAS prior to deployment to calculate the sampling rate for gas-phase compounds. DC correction is particularly useful for providing comparable data for samplers deployed in different environments and subject to different meteorological conditions, like wind speed (Moeckel et al., 2009). However, both methods have disadvantages. First, the calibration using the AAS requires too much equipment and samples to be implemented at all locations. Meanwhile, due to the variation of wind speed,

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temperature, and other environmental factors, it is inappropriate to employ the same sampling rate at different sites. Second, the sampling rate gained by DCs method is not the real sampling rate, for its hypothesis assumes that the compound sampling rate is exactly equal to the DC loss rate, which is debatable (Supplementary information, SI, Section S2.3). Moreover, DCs must have characteristics that are similar to the target compounds (such as ^{13}C -marked target compounds), and the recoveries of DCs must be at least within 20–80% (Soderstrom and Bergqvist, 2004). The DC approach is also limited by the cost and commercial availability of the appropriate compounds and the need for mass spectrometric analysis. Melymuk et al. (2011) also suggested that calibration of PAS sampling rates could be more accurately achieved using a low-volume AAS rather than DCs since the former can measure gas- and particle-phase compounds. Although there are many uncertainties in the calibration of PASs, in some situations, they may be the only option, especially if several concurrent samples are required at different locations. Therefore, we need to further improve passive air sampling technology.

The present study established an improved correction method for using a PAS to assess the distribution of PCNs in the eastern Pearl River Delta (PRD), South China. As a tributary of the Pearl River, the Dongjiang River (or East River), which is located in the eastern part of the PRD, supplies fresh water to many cities, including Guangzhou, Dongguan, Shenzhen, and Hong Kong. The highly intensive industries in this region are associated with the emission of various chemicals that may pose a potential pollution to the river and the ecosystem. However, there is a general lack of information regarding the levels and fate of PCNs in this region. This research aimed to use a newly improved correction method for a PAS to evaluate the PCN air contamination within the Dongjiang River basin of the PRD. The improved calibration method will be valuable for perfecting the correction of passive air sampling.

2. Materials and methods

2.1. Sampling, sample preparation, and analysis

PUF disks (14.0 cm diameter; 1.30 cm thick; surface area, 365 cm²; mass, 3.40 g; volume, 200 cm³; density, 0.0170 g cm⁻³) were pre-cleaned, spiked with DC standards (^{13}C -PCB 28, 52, 101, 138, 153, and 180), dried, and stored at $-20\text{ }^\circ\text{C}$ until deployment. Spiking was conducted 3 days before deployment to encourage a homogeneous distribution of the DCs within the disk (Moeckel et al., 2009). Passive air samplers (PUFs) were deployed at 19 sites (Fig. 1a; Table S1) within the eastern PRD during winter (January 1st to March 10th, 69 d) and summer (July 1st to September 8th, 70 d) of 2010. After the deployment, the PUF disks were Soxhlet extracted, purified, and analyzed by gas chromatography electron capture negative-ion mass spectrometry. Tri- to hexa-CN were quantified in this study. Details and QA/QC are showed in SI.

2.2. Improved correction method for PUF

2.2.1. Correction method based on active air sampling

The capture of PCNs by our PUF within 75 days after deployment was in the linear uptake phase (Fig. S1). The calculation method is presented in SI. The PUF sampling rates of different PCN homologue groups (tri- to hexa-) and of selected PCN congeners measured using active air sampling varied widely between homologue groups (3.0–11.6 m³ d⁻¹, Table S2). As reported (Chaemfa et al., 2009), PUF samplers can capture the particle-bound compounds, but only part of the fine/ultrafine fraction capable of penetration and collection on the PUF disk (Klanova

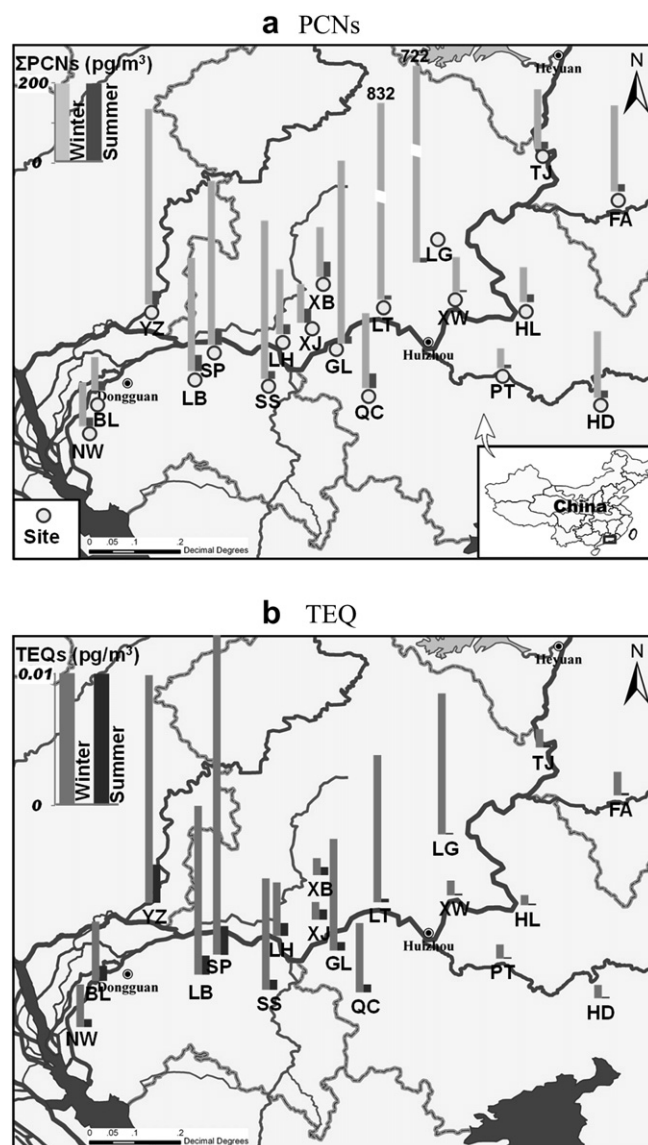


Fig. 1. Sampling locations, spatial and seasonal distributions of the PCN air concentrations. (a. ΣPCNs ; b. TEQ).

et al., 2008). Thus, using both gaseous and particle concentration to calculate the sampling rate of PUF disk may also cause a deviation. Since the particle-associated PCNs were mostly below the detection limit in this research suggesting particle-associated fraction of PCNs is not significant. Thus, the results of active air sampling contained only the gas-phase concentrations of PCNs, which made the sampling rates of different PCN homologue groups systematically increased with the molecular weight. Our sampling rates were comparable to the results of Shoeib and Harner (2002) and of Mari et al. (2008).

2.2.2. Correction method based on depuration compounds

The calculation method based on DCs is presented in SI. The PUF sampling rates (R) were calculated by the loss of DCs after 75 days of deployment, as listed in Table 1. $^{13}\text{C}_{12}$ -PCB 180 was used as a stable DC for correcting the losses of DCs in the PUF disks.

2.2.3. Improved joint-correction method

The two main correction methods using the sampling rate obtained from the AAS or the DCs added, both have advantages and

Table 1
PUF sampling rates based on the recoveries of DCs and the correction coefficients for individual homologue groups.

	¹³ C-PCB28	¹³ C-PCB52	¹³ C-PCB101	¹³ C-PCB153	¹³ C-PCB138
$K_{\text{PUF-A}}^{\text{a}}$ ($\text{m}^3 \text{g}^{-1}$)	81.4	120	345	991	1220
Rate ^b ($\text{m}^3 \text{d}^{-1}$)	5.6 ± 0.2	4.4 ± 0.2	4.0 ± 0.4	3.0 ± 0.1	3.1 ± 0.5
r^{c}					
Tri-PCNs	0.5	0.7	0.7	1.0	1.0
Tetra-PCNs	0.9	1.1	1.2	1.6	1.6
Penta-PCNs	1.5	1.9	2.2	2.9	2.8
Hexa-PCNs	2.1	2.6	2.9	3.9	3.7

^a $K_{\text{PUF-A}}$ was assumed to be constant in different sampling periods.

^b ¹³C-PCB 180 was used as the stable-DC.

^c r = Sampling rate calculated using active air sampling/sampling rate calculated using DC (rate by active air sampling is listed in Table S2).

disadvantages (see the introduction). The new, improved calibration method was based on the joint-correction used with both the AAS and DCs. Generally, we first use these two methods to obtain the passive air sampling rate (R_{PUF} and R_{DC}) at a common site, respectively. Then, we assume that the ratio of two sampling rates ($r = R_{\text{PUF}}/R_{\text{DC}}$) is constant, despite the variation of sampling sites. Therefore, only by obtaining the R_{DC} by deploying the PUF disks spiked with DCs, can a more accurate sampling rate (R_{PUF}) according to the coefficient (r) at the specific site be obtained. The correction coefficients (r) for different PCN homologue groups that were calculated using the different DCs added (¹³C₁₂-PCB 28, 52, 101, 153 and 138) are also listed in Table 1.

3. Results and discussion

3.1. Sampling rates of PUF

The recoveries of six ¹³C-labeled DCs at 19 sampling sites during two deployment periods (53–100% in winter; 15–99% in summer) are listed in Table S3. According to these recoveries, the PUF sampling rates based on a correction method established by Moeckel et al. (2009) ranged from not available to $6.0 \text{ m}^3 \text{d}^{-1}$ (Table S4). ¹³C-PCB 180 was used as the stable DC. Previous studies have indicated that lower DC recoveries are more useful than higher values because they allow for more accurate determinations of the sampling rate, as they are less susceptible to analytical uncertainty. Due to their lower $K_{\text{PUF-air}}$ values, lower molecular weight DCs experience a more substantial mass transfer from the PUF disk to ambient air (Pozo et al., 2006). The original DC requirement demands that the DC losses be within 20–80% (Huckins et al., 2002). The criteria for the use of DCs under the Global Atmospheric Passive Sampling Network (GAPS) require that the sampling rate be based on the DCs whose recoveries are less than 60% (Moeckel et al., 2009). To minimize the influence of the analytical uncertainty and also to distinguish differences in the loss from the analytical variability clearly, the strict criteria for GAPS was chosen in our research. Only the results of most of the ¹³C-PCB 28 and some of the ¹³C-PCB 52 meet the strict DC requirements (Table S3). The calibration sampling rates based on the correction coefficients of ¹³C-PCB 28 and 52 are comparable to each other at the individual sites (Tables S5 and S6). The rates based on ¹³C-PCB 52 were not available at some sites, so ¹³C-PCB 28 was chosen as the calculation DC.

Table S5 shows that the sampling rates were higher in summer (0.7 – $12.4 \text{ m}^3 \text{d}^{-1}$) than in winter (0.1 – $5.2 \text{ m}^3 \text{d}^{-1}$), which is consistent with the fact that the wind speed was usually higher in summer, especially during the typhoon periods. Previous studies have revealed that wind speed can significantly affect the sampling rate, although PUF disk is usually deployed in protective chambers to dampen the effect of wind. Tuduri et al. (2006) suggested that

the uptake rate increased sharply with the wind speed $>3.5 \text{ m s}^{-1}$. Klanova et al. (2008) found that sampling rates increased by a factor of approximately 2 with a wind speed range of 1.5 – 5.5 m s^{-1} . The sampling rates also showed spatial variation due to the difference of meteorological factors (e.g., temperature). Our results suggested that it was inappropriate to use the same sampling rate at different locations at different periods, making it crucial to add DCs to correct for the environmental effects and to improve the correction method.

The rate calculated using the AAS requires too much equipment to perform at each sampling site, although it is the most reliable way to gain the sampling rates for each compound; meanwhile, the rate obtaining using DCs has too many limitations, such as: the discrepancy or deviation between DC loss rate and the true sampling rate, the assuming that DC escape rate is exactly equal to the PUF sampling rate, the properties of DCs which need to be similar to those of the analytes to ensure the mass transfer coefficients and PUF-air partition coefficient are comparable, the various DC types or numbers to cover all the analytes, and the criteria of the DC recoveries, although it can convey more information about the variation of environmental factors. Our improved method, according to the joint calibration using the AAS and DCs, can make full use of the advantages and bypass the disadvantages of both individual methods. Instead of exactly equaling, we believe that the DC escape rate is correlated with the PUF sampling rate to some extent, therefore a correlation coefficient is needed to correct the DC escape rate. Thus, our improved method can provide a more accurate sampling rate than the DC method alone in a feasible and conventional way and can also present the difference in the sampling rate at different sites caused by various environmental factors. Moreover, for the joint method, DCs act as a correction factor, so their properties are not necessary to be similar to the target analytes. The sampling rate of PUF is affected by mass transfer coefficient, which mainly depend on PUF material, compounds' characters, and meteorological parameter. For the same PUF sampler using for the same targets, the sampling rate mostly depends on the environment factors, which can be corrected by the DC recoveries. The sampling rates calculated using the improved method are comparable to the rates of Moeckel et al. (2009), Wong et al. (2009), and Pozo et al. (2004, 2006).

3.2. Spatial and seasonal trends of PCN air concentrations

3.2.1. Spatial distribution of PCN air concentrations

Fig. 1a shows the air concentrations of the total PCNs (ΣPCN , representing tri- through hexa-congeners) at 19 sites according to the joint-correction method. The ΣPCN ranged from 51.7 to 832 pg m^{-3} , with an average of $273 \pm 225 \text{ pg m}^{-3}$ in winter, and from 6.4 to 42.6 pg m^{-3} , with an average of $24.3 \pm 10.9 \text{ pg m}^{-3}$ in summer. The highest average value of the two sampling periods was found in LT (421 pg m^{-3}), while the lowest was found in PT (30.6 pg m^{-3}). Most of the high levels were located in or near the highly industrialized area of Dongguan City, suggesting that highly industrialized area may have more PCN sources.

The PCN values for air in the summer are remarkably close to the measurements in the Great Lakes (0.3 – 52.1 pg m^{-3}) (Harner et al., 2006b) and in the GAPS study (N.D. – 32 pg m^{-3}) (Lee et al., 2007) using a PAS. However, the values in winter were much higher than those in these studies but were comparable to the results measured in the industrial area of Barcelona (228.8 – 621.8 pg m^{-3} , using an AAS) (Mari et al., 2008) and in the semirural area outside Lancaster (73.4 – 223 pg m^{-3} , using an AAS) (Lee et al., 2000).

The PCN-corresponding TEQ (sum of CN 35, 38/40, 50, 54, 56, 57, 63, 66/67, 64/68, 69, 71/72), based on the relative potency factors (RPFs) summarized by Noma et al. (2004), ranged from 0.82 to

26 fg m^{-3} in winter, with an average of $6.7 \pm 6.9 \text{ fg m}^{-3}$, and from 0.12 to 3.1 fg m^{-3} in summer, with an average of $0.78 \pm 0.80 \text{ fg m}^{-3}$ (Fig. 1b). As expected, high levels of TEQ were also mainly located in Dongguan City. The TEQ values of the PCNs in summer are consistent with the results in the semirural area outside Lancaster (0.36–3.6 fg m^{-3} , using an AAS) (Lee et al., 2000), while the values in winter were slightly higher. Furthermore, the TEQ of PCNs in our research was comparable to the TEQ of dioxin-like PCBs (0.6–36.5 fg m^{-3}), but lower than the TEQ of PCDD/Fs (7.3–579 fg m^{-3}) in the air of Hong Kong nearby (Choi et al., 2008).

3.2.2. Seasonal distribution of PCN air concentrations

The seasonal trend showed that the PCN and TEQ air concentrations were both remarkably higher in winter than in summer (Fig. 1). The different removal efficiency, as well as the different emission sources, during summer and winter may be mainly responsible for the seasonal variation. In the study area, summer is characterized by a higher temperature, stronger wind, and heavy rains, while winter is cool, dry, and less windy. Usually, a high temperature can enhance the volatility of PCNs from the volatilization sources. However, instead of high concentrations, low concentrations of PCNs in the air were observed in summer. Heavy precipitation and strong wind, especially during typhoon periods, can increase the deposition and diffusion, which may finally cause the PCN air concentrations to decrease in summer. Our concurrent deposition study (higher in summer and lower in winter) also supports this hypothesis (Wang et al., 2012). Meanwhile, the increasing of biomass burning during harvest time in winter may also enrich the air levels of PCNs in winter, which need further study.

3.3. Homologue pattern of PCNs

Tri-CNs was the most dominant homologue group in almost all samples, followed by tetra-, penta-, and hexa-CNs, based on the chlorine atom number (Fig. S2). The mass compositions of the PCN homologue groups also varied substantially with seasons ($p < 0.05$), especially for tri- and tetra-CNs. The compositions for tri-, tetra-, penta-, and hexa-CNs were 72%, 20%, 6%, and 2% in

winter and 64%, 25%, 8%, and 3% in summer, respectively. The percent composition of tri-CNs was elevated during the colder winter and was reduced during the warmer summer. Conversely, the tetra-CNs to hexa-CNs showed the opposite effect, probably reflecting the reduced volatility (lower evaporation from primary sources or higher adsorption to particle phase) of higher molecular weight PCNs at cold temperatures (Harner and Bidleman, 1998; Harner et al., 2006b). Similar observations were made by Lee et al. (2005b) and Harner et al. (2006b).

3.4. Combustion input of PCNs

Emissions from historical usage and unintentional production through combustion or thermal processes are the two main sources of PCNs (Falandysz, 1998; Harner et al., 2006b). Previous studies have indicated that the contribution of combustion-associated PCNs to contemporary PCN air burdens is increasing (Helm et al., 2004; Lee et al., 2005a; Harner et al., 2006b; van der Gon et al., 2007). Combustion-related congeners (e.g., CN 52/60, 51, 54, and 66/67) have been discovered to be minor or absent in the Halowaxes and PCB technical mixtures compared with incineration and other industrial thermal processes (Yamashita et al., 2000; Meijer et al., 2001; Helm and Bidleman, 2003). Therefore, the fraction of combustion PCNs to the total PCNs could provide evidence for the importance of combustion sources (Lee et al., 2007).

The PCN congener profile (each congener relative to its respective homologue group) based on the average value of all samples is shown in Fig. 2a. This profile is compared with that of Halowax 1014 (Fig. 2b) to assess the contribution of combustion processes to the contamination of air with PCNs. The combustion-related congeners, identified as predominant or enriched within their homologue group in the gas or ash derived from combustions, are represented by the gray bars. The black bar represents CN 24, the most abundant congener, which is considered to be associated with coal and wood combustion (Lee et al., 2005a). However, CN 24 was also found to be rich in Halowaxes and PCB technical mixtures (Yamashita et al., 2000; Helm and Bidleman, 2003; Noma et al., 2004), making it impossible to be the combustion marker. Thus, when we calculated the contribution of combustion PCNs, CN 24 was not used. Fig. 2

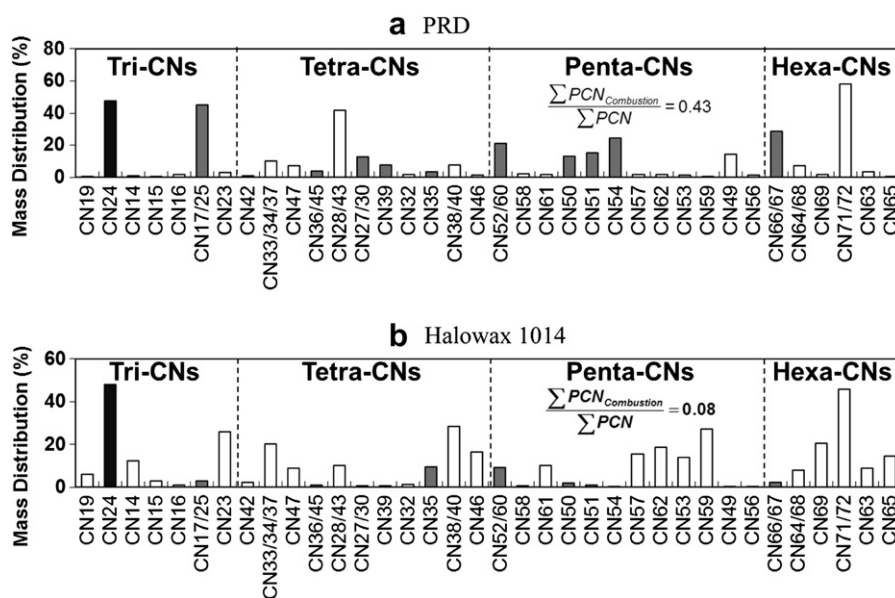


Fig. 2. Congener profiles (contribution of each congener to its respective homologue group) based on the average value of all samples. (a. PRD; b. Halowax 1014. The gray bars represent the combustion-related congeners, while the black bar represents CN 24, which was related to coal and wood combustion. The combustion-related PCNs used in the formula included CN 17/25, 36/45, 27/30, 39, 35, 52/60, 50, 51, 54, and 66/67, but not CN 24).

indicates that within each homologue group, combustion-associated PCNs were the most dominant congeners, especially in tri-CN (45%) and penta-CN (74%). The congener profiles for the 4Cl and 5Cl homologue groups from the present study are similar to those from a study in Kuwait city (Lee et al., 2007), but they are both markedly different from those for Halowaxes, suggesting that the PCNs in these two areas may have the same sources other than emissions from the commercial use of PCNs.

The contributions of combustion-related congeners (tri-CN to hexa-CN) to total PCNs ($\Sigma\text{PCN}_{\text{combustion}}/\Sigma\text{PCN}$) in the Dongjiang River basin of the PRD and Halowax 1014 are also shown in Fig. 2. The percentage for PRD is 0.43, which is considerably higher than that for Halowax 1014 (0.08). Previous research (Lee et al., 2007) had indicated that the fractions for Halowaxes are less than 0.11 and that those for fly ashes from combustion are no less than 0.5 based on the data provided by Noma et al. (2004) and Helm and Bidleman (2003), respectively. The fraction for our study area (0.43) is slightly below 0.5, but significantly higher than 0.11, indicating that the contribution of combustion sources to the PCN air burden has already become significant compared with the historical evaporations.

4. Conclusions

The improved correction method based on the joint calibration of active air sampling and DCs can provide a more accurate sampling rate than the DC method itself, and it can identify the site-specific sampling rate caused by various environmental factors. Moreover, since the added DC acts as a correction factor, it is not necessary for its properties to be similar to the analytes.

Higher concentrations of PCNs were mostly discovered in the highly industrialized areas, implying that there are more PCN sources in those areas. The reduction of PCN levels in the air in summer may be due to the high deposition value of PCNs caused by frequent precipitation. CN 24 was the most dominant congener, making tri-CN the most dominant homologue group. High concentrations of CN 24 may suggest that there are coal and wood combustion inputs of PCNs in the study area. The high composition of other combustion-related PCNs may also indicate that the contribution of combustion sources to the contemporary PCN air contamination has become significant compared with historical emissions. For this reason, more attention should be paid to combustion and incineration to avoid the unintentional generation of PCNs in the future.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2012.01.043

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